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Synthesis of Ti(IV) complexes of donor-functionalised phenoxy-imine tridentates and their evaluation in ethylene oligomerisation and polymerisation†

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A number of analogues of the Mitsui Chemicals ethylene trimerisation system (**IV**) have been explored, in which one of the donor atoms have been modified. Thus, a series of mono-anionic tridentate phenoxy-imine (3-(*t*-butyl)-2-(OH)-$C_6H_4C{=}N(C(CH_3)_2CH_2OMe)$ **1**, 3-(adamantyl)-2-(OH)-$C_6H_4C{=}N(2'\text{-}(2''\text{-}(SMe)\text{-}C_6H_4)\text{-}C_6H_4)$ **2**, 3-(*t*-butyl)-2-($OSiMe_3$)-$C_6H_4C{=}N(C(CH_3)_2CH_2OMe)$ **3**) or phenoxy-amine (3,5-di(*t*-butyl)-2-(OH)-$C_6H_4CH_2\text{-}N(2'\text{-}(2''\text{-}(OMe)C_6H_4)\text{-}C_6H_4)$ **4**) ligands have been prepared and reacted with $TiCl_4$ or $TiCl_4(thf)_2$ to give the mono-ligand complexes **5–7**. The solid state structures of compounds **4–6** have been determined. Complexes **5–7** have been tested for their potential as ethylene oligomerisation/polymerisation systems in conjunction with MAO activator and benchmarked against the Mitsui phenoxy-imine trimerisation system **IV**. While the phenoxy-amine complex **6** shows a propensity for polymer formation, the phenoxy-imine complexes **5** and **7** show somewhat increased formation of short chain LAOs. Complex **5** is selective for 1-butene in the oligomeric fraction, while **7** displays liquid phase selectivity to 1-hexene. As such **7**, which is a sulfur substituted analogue of the Mitsui system **IV**, displays similar characteristics to the parent catalyst. However, its utility is limited by the lower activity and predominant formation of polyethylene.

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Introduction

The conversion of olefins into higher olefin feedstocks and polyolefins by transition metal catalysts is a field of research that receives continual attention from groups in both academia and industry. In more recent years, there has been a particular focus on the selective conversion of ethylene into polymer grade linear alpha olefins (LAOs) such as 1-butene, 1-hexene and 1-octene.[1–8] Such processes avoid the formation of the high molecular weight fractions of LAOs, which are typically formed during full-range processes that yield Schulz–Flory or Poisson distributions of products, and are of lower value than their short chain counterparts. While chromium is the transition metal present in the majority of catalysts reported for the selective trimerisation of ethylene, several examples of systems based on titanium have appeared in the literature.[1,4,5,9–14]

Phenoxy-imine ligands are a particularly attractive ligand system due to the high degree of functionalisation that can be incorporated through simple synthetic methods. As such, it is unsurprising that they have been employed as ligands in ethylene polymerisation systems for a wide range of metals. A particularly efficient example of such catalysts are the bis-ligated phenoxy-imine complexes of titanium and zirconium (termed FI catalysts, **I**).[15–22] Such systems are highly active and well known for their controlled olefin polymerisation/co-polymerisation. This initial discovery by Coates[21] and Fujita[18] independently has led to a wide range of studies on the bis-ligated systems.

However, examples of mono-ligated group IV complexes are less well known. Work by Lapido and co-workers and Lancaster and co-workers has demonstrated the generation of mono-ligated bidentate complexes (**II**) of Ti and Zr and shown their efficiency towards ethylene polymerisation.[23–25] More recently, examples of mono-ligated tridentate phenoxy-imine systems (**III**) have been explored in the literature.[26–37] Such compounds are reported to be efficient catalysts for ethylene polymerisation and show good incorporation for a wide variety of olefins during ethylene/olefin co-polymerisation.[28–37]

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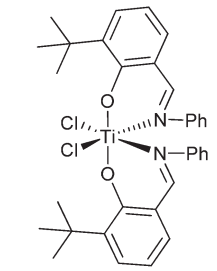
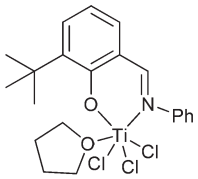
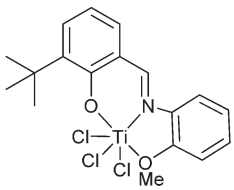
†Electronic supplementary information (ESI) available: Details of X-ray structure of S1. CCDC 902939–902942. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32465f



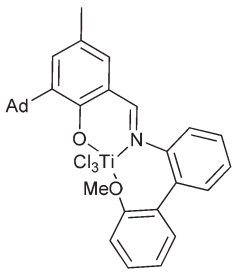
I



II



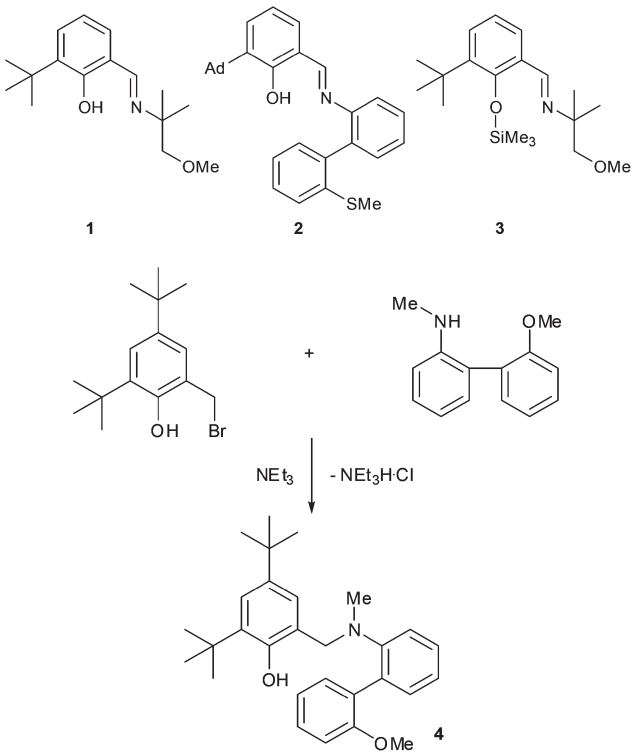
III



IV

However, until recently selective oligomerisation systems based on the phenoxy-imine ligand motif were unknown. In 2009, researchers from Mitsui Chemicals first disclosed in the patent literature a highly active trimerisation system based on this motif (**IV**).[38] The most active of these compounds have been reported to yield activities in excess of 6800 kg (mol Ti)$^{-1}$ h^{-1} bar^{-1} and 1-hexene selectivity greater than 93%.[9] While complex **IV** represents the optimised system, a large range of modifications to the ligand structure are detailed in the patent covering this work.[38]

The studies by Fujita and co-workers have thoroughly investigated the ligands effect on 1-hexene selectivity and catalyst activity by varying the sterics of 4- and 6-position of the phenoxide ring, the nature of the carbon bridge between the imine nitrogen and the pendant donor, the nature of the ether substituent and atom choice for the pendant donor for atoms with a hard Lewis basic nature.[9,38] However, in both the academic and patent literature there are no studies exploring analogous complexes containing amines in place of imines or including soft Lewis bases as donors. Herein we report the preparation and characterisation of such a series of analogues of the Mitsui trimerisation system and their catalytic behaviour in conjunction with methylaluminoxane (MAO).



Scheme 1 Synthesis of ligand **4**.

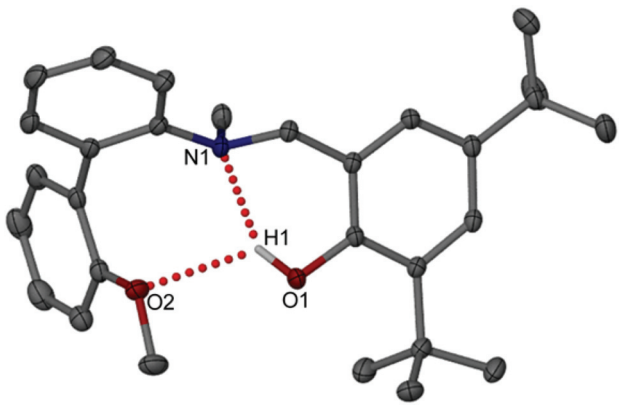
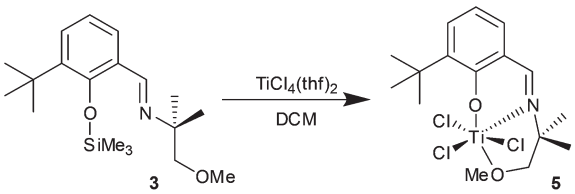


Fig. 1 Molecular structure of **4**. Thermal ellipsoids are shown at the 50% probability level. All methyl, methylene and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): O1–H1 0.90(2), H1···O2, N1 2.41, 2.03, O1–H1···O2, N1 123.9, 147.8.

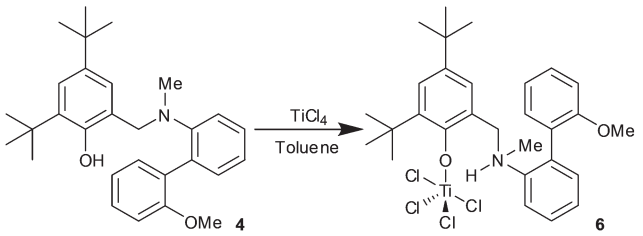
Results and discussion

Synthesis and structures

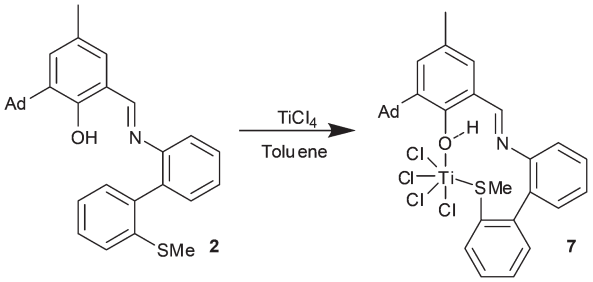
The salicylaldimine ligands **1** and **2** were prepared through the condensation reaction of the appropriate salicylaldehyde with the desired amine. Ligand **1** was further derivatised to give the trimethylsilyl ether **3**; these ethers have been shown to be more selective in generating 1 : 1 complexes when reacted with $TiCl_4(thf)_2$.[24,25] Ligands of the type **4** would typically be prepared by the reduction of the appropriate salicylaldimine, however this methodology was found to be low yielding and require extensive purification.[32,39–41] Preparation of ligand **4** was readily achieved by the reaction of 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide with 2-(2′-methoxyphenyl)-*N*-methylaniline in the presence of triethylamine (Scheme 1) by an analogous literature procedure.[42] In all cases the ligand systems have been characterised by ^{1}H and ^{13}C NMR and mass spectra. In addition, crystals of ligand **4** were grown from a saturated solution in petroleum spirits and the structure determined by X-ray crystallography (Fig. 1). The solid state structure clearly shows the intramolecular H-bond interactions between the



Scheme 2 Synthesis of complex **5**.



Scheme 3 Synthesis of complex **6**.



Scheme 4 Synthesis of complex **7**.

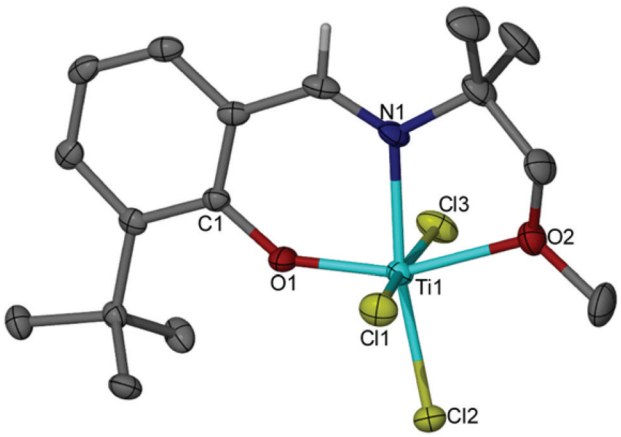


Fig. 2 Molecular structure of **5**. Thermal ellipsoids are shown at the 50% probability level (one of two, similar molecules shown). A disordered lattice DCM molecule is omitted for clarity, as are all methyl, methylene and aromatic-ring hydrogen atoms. Selected bond lengths (Å) and angles (°): Ti–$O_{phenoxide,ether}$ 1.783(3)–1.785(3), 2.122(4)–2.124(3), Ti–N 2.160(4)–2.167(4), Ti–Cl 2.2892(16)–2.3363(15), O–Ti–$N_{phenoxide,ether}$ 84.29(16)–84.71(16), 74.13(15)–74.25(14), O–Ti–O 158.48(16)–158.81(16), X–Ti–$Y_{cis(acyclic),trans(acyclic)}$ 84.68(10)–104.69(12), 169.41(6)–172.73(6), $C_{phenoxide}$–O–Ti 143.5(3)–143.8(3).

phenolic hydrogen and both the amine and methoxy functionalities.

The dehalosilylation reaction of trimethylsilyl ether **3** with $TiCl_4(thf)_2$ proceeded cleanly to yield complex **5** in good yield (Scheme 2). All the titanium complexes discussed herein have been characterised with ^1H and ^{13}C NMR spectroscopy and elemental analysis. Crystals suitable for X-ray diffraction were grown by evaporation of a concentrated dichloromethane solution of **5** (Fig. 2). The complex displays a distorted octahedral geometry with a meridional arrangement of the tridentate ligand. This arrangement is well known for mono-ligated salicylaldimine complexes of titanium bearing one to two carbon linkers between the imine nitrogen and the donor moiety.[26,27,31,33–37] Comparison of the key bond lengths with a previously reported analogous system derived from (1*R*,2*S*)-(−)-1-aminoindanol[26] shows good agreement between the Ti–$O_{phenoxide}$ (1.784(3)–1.785(3)/1.7924(16) Å) and Ti–N bond lengths (2.160(4)–2.1674(4)/2.1570(19) Å) while the Ti–O_{donor} (2.122(4)–2.124(3)/2.0514(17) Å) is somewhat lengthened in our complex; a result which may be attributed to the reduced Lewis basic nature of the methoxy- *versus* hydroxyl-functionality. Attempts to prepare an analogous complex where the 6-position of the phenoxide ring is unsubstituted were also undertaken, however instead of the desired mono-ligated complex a bis-ligated system was isolated (S1†), the crystal structure of which is shown in the ESI.†

Work by researchers at Mitsui Chemicals has shown that the reaction between $TiCl_4$ and salicylaldimine ligands with extended carbon chains (greater than four) between the imine moiety and a donor moiety can react cleanly and efficiently to yield mono-anionic tridentate titanium complexes.[9,38] The reaction of ligands **2** and **4** with $TiCl_4$ has been undertaken in toluene to yield the complexes **6** and **7** as dark red solids in good yields (Schemes 3 and 4). The ^1H NMR of complex **6** in CD_2Cl_2 is somewhat complicated. The –N(CH_3)*H*– resonance occurs as a broad singlet at δ 8.05; this proton in turn couples to both the amine methyl group yielding a doublet at δ 3.75 (^3J = 5.1 Hz) and to the methylene protons. Furthermore, the methylene protons, along with the NH proton, are diastereotopic presenting as an ABX spin system with pseudodoublets at δ 4.28 and δ 5.70 ($^2J_{A,B} \approx 12.8$ Hz and $^3J_{A,X/B,X} \approx 2.1$ and 9.9 Hz), the assignment of the methylene protons was further confirmed using COSY spectroscopy. Crystals suitable for X-ray diffraction were prepared by evaporation of a saturated dichloromethane solution of complex **6** (Fig. 3). The solid state structure shows the ligands arranged in a slightly distorted trigonal bipyramidal geometry around the titanium centre. The distortion around the titanium centre is apparent in the Cl3–Ti–Cl4 bond angle (175.25(3)°), O1–Ti1–Cl2 bond angle (116.60(7)°) and O1–Ti1–Cl4 bond angle (94.75(7)°). Additionally, the Ti–Cl_{ax} bond lengths (2.3114(8)–2.3716(8) Å) are somewhat lengthened compared to the Ti–Cl_{eq} bond lengths (2.2554(8)–2.2695(8) Å); the longest of which is the Ti–Cl3 bond (2.3716(8) Å). This lengthing can be attributed to the H1···Cl3 interaction (2.63 Å) reducing the hard Lewis basicity of the chloro ligand and thus reducing its capacity to donate to the titanium metal centre. The ammonium proton also feels a hydrogen bonding

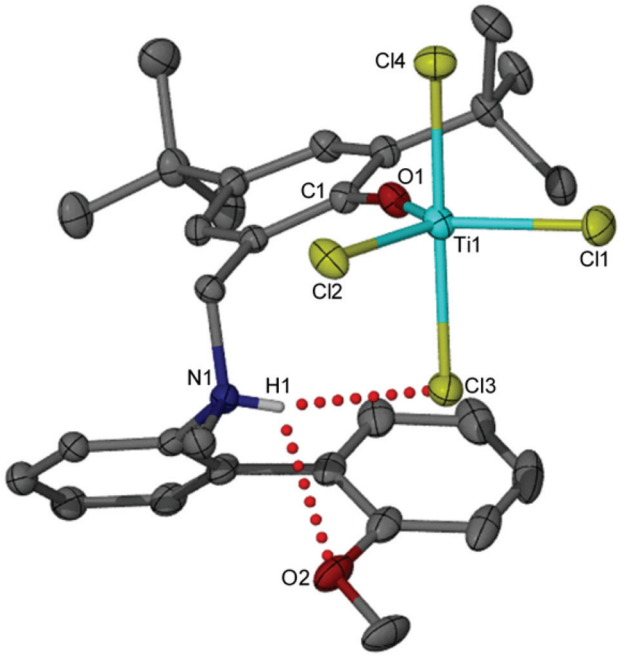


Fig. 3 Molecular structure of **6**. Thermal ellipsoids are shown at the 50% probability level (lattice solvent DCM and toluene are omitted). All methyl, methylene and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–O 1.7573(18), Ti–Cl 2.2554(8)–2.3716(8), N1–H1 0.77(4), H1···O2, Cl3 2.50, 2.63, O–Ti–$Cl_{eq/ax,eq/eq}$ 89.91(7)–94.75(7), 116.60(7)–120.98(7), Cl–Ti–$Cl_{eq/ax,eq/eq,ax/ax}$ 87.24(3)–89.88(3), 122.24(3), 175.25(3), Ti1–O1–C1 167.23(17), N1–H1···O2,Cl3 116.9, 147.0.

interaction with the methoxy substituent (2.50 Å). Trigonal bipyramidal geometries for titanium are, to the authors' knowledge, relatively rare with complexes typically preferring to assume either a piano stool type ligand arrangement or an octahedral geometry *via* coordination of pendant donors or chloro-bridging forming oligomeric species. However examples for Ti(II) and Ti(III),[43] cyclopentadienyl stabilised Ti(IV) and Zr(IV)[44,45] and Ti(IV) alkoxy[46] and amido[47] ligand systems have previously appeared in the literature. Overall, a titanate complex has been generated which is charge stabilised intramolecularly by the ligands cationic ammonium moiety. As such, it is apparent that the amine functionality of **4** acts as a base capturing the proton generated during synthesis; analogous reactions have previously been noted for group IV metals.[48–50] Previous work has shown that analogous compounds readily liberate hydrochloric acid in the presence of triethylamine, however attempts employing complex **6** yielded complex mixtures of **6**, **6**-HCl and triethylamine hydrochloride. Attempts to prepare HCl free **6** by deprotonation of the ligand with *n*-butyllithium or $NaN(SiMe_3)_2$ and subsequent reaction with $TiCl_4$ yielded only an intractable mixture with no isolable species.[51] Similarly, preparation of the trimethylsilyl ether derivative of **4**, upon introduction to $TiCl_4$, yielded the same result.

The ^{1}H NMR of complex **7** in CD_2Cl_2 shows a broadened singlet at δ 8.73, shifted significantly upfield from the free ligand where it occurs at δ 13.11, which integrates for one proton and has been assigned to the hydroxy proton of the ligand system, however the imine proton does not show the characteristic splitting that has been reported for analogous complexes of Ti wherein the proton is associated with the nitrogen centre.[48] This, and the considerable broadening of the NMR signals, is highly suggestive that the ligand is associated with the titanium centre but that deprotonation has not occurred, a fact that is consistent with the elemental analysis. However, without a solid state structure it is hard to speculate on the exact geometry and as such the connectivity shown in Scheme 4 is tentative.

Ethylene oligomerisation and polymerisation

The titanium complexes **5–7** have been screened for ethylene oligomerisation/polymerisation activity in combination with methylaluminoxane (MAO). While complexes **6** and **7** have been prepared as what are essentially the hydrochloric acid adducts of the desired mono-anionic tridentate systems, analogous systems have been shown in the literature to readily liberate the acid under basic conditions.[41,48,50] Furthermore, the inventors of the highly active Mitsui system demonstrate in their patent literature that the reaction mixture of the ligand and $TiCl_4$ can be employed as an olefin oligomerisation catalyst without purification.[38] As such it is easy to conceive a similar process upon introduction of the alkylaluminium co-catalysts to our isolated complexes, to yield the desired mono-anionic tridentate systems.

The results of the catalytic testing are shown in Table 1. Complex **IV** has been included as a benchmark for our novel systems. Under optimised conditions this complex has been reported to yield 1-hexene selectivities in excess of 93% and activities greater than 6800 kg (mol Ti)$^{-1}$ h^{-1} bar^{-1}.[9] Under our non-optimised conditions complex **IV** yielded a significantly lower activity, albeit still highly active, than that reported in the literature (Table 1, entry 1).[9] The selectivity of the catalyst in our hands compares favourably with the previously reported values including high selectivity towards 1-hexene and low polymer formation. The majority of the C_{8+} fraction consisted of three C_{10} isomers which is consistent with previous reports wherein 1-hexene and ethylene are cotrimerised to form branched oligomers.[9] However, unlike the original reports by the researchers at Mitsui Chemicals we noted small portions of 1-butene (0.5%), 1-octene (0.3%) and $C_{12}H_{24}$ (0.1%) and $C_{14}H_{28}$ (0.1%) branched isomers amongst the liquid fraction. The C_{14} fraction is readily explained by the co-trimerisation of two molecules of 1-hexene with one molecule of ethylene. To the contrary, the C_{12} isomers may result from co-trimerisation of 1-octene with two ethylene molecules or the dimerisation of two 1-hexene molecules; given the relatively low abundance of 1-octene in the catalysis mixture, formation through the dimerisation route seems the most likely. In order to confirm that the C_{12} isomers were the result of dimerisation of 1-hexene, a catalytic run was performed wherein upon activation of the catalyst a portion of 1-hexene was added but no ethylene was introduced to the system. Upon quenching and analysis of the

Table 1 Ethylene oligomerisation/polymerisation with **5–7** and MAO[a]

Entry	Catalyst	MAO equiv.	Activity[b]	% 1-Butene	% 1-Hexene	% 1-C_{8+}	% Polyethylene
1	**IV**	300	236	0.5	87.5	9.0	3.0
2	**5**	300	0.6	7.4	0.7	—	91.9
3	**6**	300	14	1.1	1.6	1.0	96.3
4	**7**	300	24	0.5	11.3	1.3	86.9
5	**7**	400	29	0.3	9.7	0.3	89.7
6	**7**	1000	28	0.3	3.5	0.3	95.9
7	**7**	200	7	Trace	24.8	—	75.2
8	**7**	100	13	0.9	0.3	1.3	97.5

[a] Conditions: 20 μmol catalyst loading, toluene (50 mL), 5 bar ethylene, 30 °C, 30 min. [b] kg product {(mol metal) h bar}$^{-1}$.

liquid oligomers a series of dimers, trimers and tetramers were detected, of which the dimers were the most prevalent. However, significant isomerisation of the residual 1-hexene into two new isomers was also noted; such isomerisation is not evident in the presence of ethylene and as such it is hard to draw firm conclusions on the exact mode by which the C_{12} isomers are formed.

In all cases the novel precatalysts show reduced activities and selectivities in comparison to the parent system for ethylene trimerisation. Complex **5** showed the lowest activity of all the complexes that were screened (Table 1, entry 2) and while a considerable amount of polymer was formed the liquid phase showed interesting selectivity towards 1-butene (7.4% overall). Similar mono-ligated bidentate phenoxy-imine compounds have been shown to dimerise ethylene in combination with some alkylaluminiums.[52] Previous reports have suggested that short alkyl-chains (less than four carbons) between the imine functionality and the donor moiety, as is the case in this complex, can lead to a selectivity shift from ethylene oligomerisation to polymerisation.[38] In a related study of such short chain complexes it was found that having a hard Lewis basic donor such as an ether considerably impeded the activity of catalyst when compared to softer Lewis basic donors and as such may be the reason for the low activity.[33] Complex **6**, while being moderately active for ethylene polymerisation, showed unremarkable selectivity in the liquid phase (Table 1, entry 3) yielding a series of even-numbered linear alpha olefins from C_4–C_{28}. From the catalytic data it appears that the conjugation between the phenoxide anion and the imine moiety, present in **IV**, plays an important role in stabilising the catalyst towards ethylene trimerisation, although structural changes brought about by introduction of the amine may also play a role.

Complex **7**, which is the most structurally similar to the Mitsui system **IV**, under the initial conditions gave the greatest selectivity towards 1-hexene (11%) of the novel systems explored herein (Table 1, entry 4), with the remaining product predominately consisting of polymer. It was noted that premixing of the precatalyst with MAO changed the solution colour from a bright orange to a pale yellow which is consistent with an alkylated titanium(IV) species,[33,53] however upon completion of the catalytic run the polymer obtained a deep purple colour which dissipated in contact with air and during the polymer washing. This colour is indicative of catalyst reduction to a titanium(III) species[54] – a process which has been reported for some titanium compounds in combination with alkylaluminiums.[55,56] Tang and co-workers have previously reported that mono-anionic tridentate systems with the phenoxy-imine motif of the form [$^-$ONO] can readily stabilise the Ti(IV) metal centre in conjunction with modified MAO. In the same study analogous compounds of the form [$^-$ONS] were shown to readily undergo reduction in the presence of the same activator yielding ethylene polymerisation catalysts.[33] It is possible to suggest that a similar reduction is occurring in our system wherein the majority of the 1-hexene is formed in the initial period of catalysis and as time progresses the catalyst reduces to form a titanium(III) polymerisation species. Alternatively, upon activation it is also possible to envisage that a catalytic mixture forms wherein some of the complex remains as the titanium(IV) trimerisation species while the majority is reduced to the titanium(III) polymerisation species. Following this notion, increasing the concentration of MAO employed in catalysis from 300 to 400 and 1000 equivalents (*cf.* Table 1, entries 4–6) gave comparable activities but showed a marked reduction in 1-hexene selectivity, suggesting a reduction in the concentration of the ethylene trimerisation catalyst. In an effort to reduce the rate of reduction of the metal centre and to increase the selectivity of the catalyst to 1-hexene, a number of runs employing low MAO loadings were employed (Table 1, entries 7 and 8). Reducing the MAO loading to 200 equivalents did indeed increase the 1-hexene selectivity, although was accompanied by a reduced activity. A further reduction in MAO loading down to 100 equivalents unfortunately led to a complete loss of selectivity forming only a series of LAOs and polymer; such a change in selectivity is highly suggestive that insufficient activator is present to generate the targeted catalytic species, and perhaps a different active species is forming. To definitively ascertain whether the reduction of the titanium centre is occurring during the early stages of the reaction, or as a gradual process throughout the catalysis, a short run was performed wherein the catalyst was activated with MAO before being exposed to ethylene for 30 seconds and then being quenched with hydrochloric acid. Analysis of products showed a mixture of polyethylene (99%) and 1-hexene, which is highly

supportive of a mechanism wherein the majority of the catalyst is reduced to the titanium(III) species in the initial period of catalysis.

The formation of both short chain oligomers and polymer indicates a number of active species to be present, possibly operating *via* different mechanisms. On a number of other occasions we have observed such behaviour with Ti catalysts.[52,57] This frequently takes the form of oligomers formed *via* a metallacycle mechanism, and polymer most likely resulting from a Cossee mode of chain growth. This may, in these other cases, be likewise due to oxidation state changes of titanium, as has been suggested above, although further work is necessary to confirm this.

Conclusions

Herein we have prepared a number of analogues to the Mitsui (Ti phenoxy-imine) ethylene trimerisation system.[9] This catalyst is clearly sensitive to changes in the bridging group linking the third donor atom, the identity of this donor, and also changes to the imine donor (reduction to an amine). Of the modifications evaluated, the best result with respect to ethylene trimerisation was obtained when a thioether was introduced in place of the ether (complex 7). In this case substantial selectivity towards 1-hexene was displayed in the oligomeric products, however the formation of polyethylene still dominates. This may be due to reduction of the catalyst to Ti(III), whereas 1-hexene is expected to result from a Ti(II)/Ti(IV) cycle. Further work is required to confirm this however. This work again illustrates the tendency of Ti precatalysts to form multiple active sites following activation with MAO, and hence to display multi-mechanism behaviour. The challenge in obtaining selective oligomerisation with these systems therefore seems to lie in control of this behaviour.

Experimental

General

All manipulations were performed under an atmosphere of UHP argon (BOC gases) using standard Schlenk techniques or in an MBraun glovebox unless otherwise stated. Solvents, excluding dichloromethane, were purified by passage through an Innovative Technologies purification system and, where appropriate, stored over a sodium mirror. Anhydrous dichloromethane was purchased from Sigma-Aldrich and stored over 3 Å molecular sieves. CP grade ethylene (BOC gases) was purified by passage through a column of activated 3 Å molecular sieves and alumina. NMR spectra were recorded on a Varian Mercury Plus NMR spectrometer operating at 300 MHz (^{1}H) or 75 MHz (^{13}C) at room temperature. MAO was supplied by Albemarle as a 10% solution in toluene. Complex **IV** was prepared according to the literature method.[9]

Preparation of 2-(2′-(methylthio)phenyl)aniline. 2-Bromoaniline (3.23 g, 18.7 mmol), 2-(methylthio)phenylboronic acid (3.00 g, 17.9 mmol), palladium(II) chloride (0.32 g, 1.79 mmol), triphenylphosphine (0.94 g, 3.58 mmol) and potassium carbonate (3.69 g, 26.7 mmol) were suspended in 45 mL of toluene and heated to 100 °C overnight. The resulting brown solution was cooled to room temperature and diluted with 45 mL of deionised water. The organic phase was separated and the aqueous phase was extracted with 3 × 45 mL of toluene. The organic phases were combined, dried with sodium sulphate and the volatiles were removed under reduced pressure. The remaining brown residue was purified by column chromatography (1 : 4 ethyl acetate : petroleum spirits) to yield the title compound as a white solid in 40% yield (1.54 g, 7.14 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 6.75–7.41 (m, 8H, *aryl-H*), 3.58 (br s, 2H, NH_2), 2.38 (s, 3H, SCH_3). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 126.2, 137.6, 139.0, 144.6 (*aryl-C*$_{ipso}$), 115.7, 116.3, 125.0, 125.2, 128.7, 129.9, 130.7, 130.8 (*aryl-C*), 15.4 (S*C*H$_3$). MS (electron ionisation): *m*/*z* 215 $[M]^+$.

Preparation of 2-(2′-methoxyphenyl)-*N*-methylaniline. 2-Bromo-*N*-methylaniline (1.29 g, 6.91 mmol), 2-methoxyphenylboronic acid (1.00 g, 6.58 mmol), palladium(II) chloride (0.12 g, 0.658 mmol), triphenylphosphine (0.35 g, 1.32 mmol) and potassium carbonate (1.36 g, 9.87 mmol) were combined and degassed with five vacuum/argon refill cycles. 15 mL of toluene was added and the suspension was heated to 100 °C overnight. The resulting dark brown suspension was cooled and washed with 30 mL of brine solution. The brine solution was back extracted with 2 × 20 mL of toluene and the organic phases were combined, dried on sodium sulphate, filtered and concentrated to give a brown residue. The residue was purified by column chromatography (1 : 4 ethyl acetate : petroleum spirits) to give a white solid, which upon washing with 2 × 5 mL petroleum spirits, was identified as the title compound in 41% yield (0.57 g, 2.69 mmol). ^{1}H NMR ($CDCl_3$, 299.89 MHz): δ 7.23–7.56 (m, 3H, *aryl-H*), 6.96–7.10 (m, 3H, *aryl-H*), 6.73–6.82 (m, 2H, *aryl-H*), 3.81 (s, 1H, N*H*), 3.78 (s, 3H, OCH_3), 2.80 (s, 3H, NCH_3). ^{13}C NMR ($CDCl_3$, 75.41 MHz): δ 146.8, 157.0 (*aryl-C*$_{ipso}$), 110.3, 111.5, 117.0, 121.3, 128.7, 128.8, 129.1. 130.7, 131.6, 132.1 (*aryl-C*), 55.9 (O*C*H$_3$), 31.2 (N*C*H$_3$). MS (electrospray ionisation): *m*/*z* 214.1 $[M + H]^+$.

Preparation ligand 1. 3-*tert*-Butylsalicylaldehyde (1.54 g, 8.66 mmol), 2-methyl-3-methoxypropyl-2-amine (0.89 g, 8.66 mmol) and 3 Å molecular sieves were combined with 20 mL of diethyl ether and the bright yellow mixture was stirred overnight. The sieves were removed *via* filtration and were washed with a further 3 × 20 mL portions of diethyl ether. The organic fractions were combined and the volatiles were removed *in vacuo* to give a yellow liquid which was purified by flash distillation at 130 °C under full pump vacuum yielding the title compound as a yellow liquid in 52% yield (1.19 g, 4.53 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 14.63 (s, 1H, O*H*), 8.40 (s, 1H, N=C*H*), 7.30 (dd, J = 1.50, 6.00 Hz, 1H, *aryl-H*), 7.14 (dd, J = 1.50, 6.00 Hz, 1H, *aryl-H*), 6.79 (t, J = 7.50 Hz, 1H, *aryl-H*), 3.38 (s, 2H, CH_2–O–CH$_3$), 3.35 (s, 2H, CH$_2$–O–CH_3), 1.42 (s, 9H, C(CH_3)$_3$), 1.31 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 162.9 (N=*C*H), 119.2, 137.7, 161.3

(*aryl-C*$_{ipso}$), 117.8, 129.5, 130.3 (*aryl-C*), 81.1 (CH_2–O–*C*H_3), 60.2 (*C*(CH_3)$_2$), 59.6 (*C*H_2–O–CH_3), 35.1 (*C*(CH_3)$_3$), 29.5 (C(*C*H_3)$_3$), 24.6 (C(*C*H_3)$_2$). MS (electrospray ionisation): *m*/*z* 264.4 $[M]^+$.

Preparation of ligand 2. 2-(2′-(Methylthio)phenyl)aniline (1.03 g, 4.76 mmol) and 2-hydroxy-5-methyl-3-(1-adamantyl)-benzaldehyde (1.29 g, 4.75 mmol) were combined and heated to 120 °C overnight with stirring to give an orange solid. Unreacted starting material was sublimed by heating the reaction mixture to 240 °C under vacuum. The remaining solid was extracted with 20 mL of dichloromethane, filtered and dried under reduced pressure to give the title compound as an orange solid in 99% yield (2.20 g, 4.70 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 13.11 (s, 1H, O*H*), 8.53 (s, 1H, N=C*H*), 6.74–7.51 (m, 10H, *aryl-H*), 2.37 (s, 3H, SC*H*$_3$), 2.25 (s, 3H, aryl-C*H*$_3$), 2.04 (s, 9H, adamantyl-4,6,10-C*H*$_2$ and adamantyl-C*H*), 1.77 (s, 6H, adamantyl-2,8,9-C*H*$_2$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 163.4 (N=*C*H), 127.3, 130.7, 136.0, 137.8, 138.4, 138.6, 147.1, 158.8 (*aryl-C*$_{ipso}$), 118.6, 124.9, 125.2, 126.8, 128.5, 129.5, 130.4, 130.5, 131.1, 131.7 (*aryl-C*), 29.6, 37.5, 40.5 (*adamantyl-C*), 37.2 (quaternary *adamantyl-C*), 20.7 (Ar-*C*H_3), 15.8 (S*C*H_3). MS (electron ionisation): *m*/*z* 467 $[M]^+$.

Preparation of ligand 3. **1** (0.62 g, 2.37 mmol) was dissolved in 10 mL of petroleum spirits with stirring. The bright yellow solution was cooled to −78 °C and *n*-butyllithium (1.48 mL, 2.37 mmol, 1.6 M in hexanes) was added dropwise. Upon complete addition the resulting white suspension was allowed to warm to room temperature and stirred for 4 hours. The supernatant was then removed *via* cannula filtration and the remaining white solid was washed with a further 10 mL portion of petroleum spirits before being dried *in vacuo*. The solid was then dissolved in 10 mL of tetrahydrofuran and 2.5 mL of trimethylsilyl chloride added. The solution was then heated to 60 °C overnight. Upon cooling the volatiles were removed under reduced pressure and the remaining residue was extracted with 20 mL of petroleum spirits. Concentration of the extract gave the title compound as a yellow liquid in 38% yield (0.30 g, 0.91 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.51 (s, 1H, N=C*H*), 7.75 (dd, *J* = 1.80, 6.00 Hz, 1H, *aryl-H*), 7.37 (dd, *J* = 1.80, 6.00 Hz, 1H, *aryl-H*), 6.91 (t, *J* = 7.50 Hz, 1H, *aryl-H*), 3.36 (s, 3H, CH_2–O–C*H*$_3$), 3.32 (s, 3H, C*H*$_2$–O–CH_3), 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.26 (s, 6H, C(C*H*$_3$)$_2$), 0.33 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 129.5, 141.4, 154.8 (*aryl-C*$_{ipso}$), 154.4 (N=*C*H), 121.5, 126.5, 129.7 (*aryl-C*), 81.7 (CH_2–O–*C*H_3), 61.2 (*C*(CH_3)$_2$), 59.4 (*C*H_2–O–CH_3), 35.1 (*C*(CH_3)$_3$), 30.8 (C(*C*H_3)$_3$), 24.7 (C(*C*H_3)$_2$), 2.06 (Si(*C*H_3)$_3$). MS (electron ionisation): *m*/*z* 335 $[M]^+$.

Preparation of ligand 4. 3,5-Di-*tert*-butyl-2-hydroxybenzyl bromide (0.62 g, 2.69 mmol) and 2-(2′-methoxyphenyl)-*N*-methylaniline (0.57 g, 2.69 mmol) were combined and degassed using five vacuum/argon refill cycles. The solids were dissolved in 70 mL of tetrahydrofuran and triethylamine (0.42 mL, 2.96 mmol) was added dropwise to give a white suspension which was stirred for two hours at room temperature. The suspension was filtered and the filtrate was concentrated under reduced pressure to yield a yellow liquid. The liquid was redissolved in 50 mL of dichloromethane and washed with 3 × 60 mL portions of deionised water. The organic phase was then dried on sodium sulphate, filtered and the volatiles removed *in vacuo* to give a yellow residue which was recrystallised from 10 mL petroleum spirits at −20 °C to give compound **4** as white needles in 18% yield (0.21 g, 0.484 mmol). Subsequent concentration and recooling of the supernatant gave a second crop of **4** (0.14 g, 0.334 mmol, yield: 12%, total yield: 40%). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 9.37 (s, 1H, O*H*), 6.87–7.42 (m, 10H, *aryl-H*), 4.06 (s, 2H, C*H*$_2$), 3.79 (s, 3H, OC*H*$_3$), 2.33 (s, 3H, NC*H*$_3$), 1.31 (s, 9H, C(C*H*$_3$)$_3$), 1.25 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 121.2, 129.6, 135.5, 136.1, 140.8, 151.8, 154.2, 156.8 (*aryl-C*$_{ipso}$), 111.3, 120.8, 120.9, 123.2, 124.3, 125.2, 128.9, 129.3, 131.4, 132.3 (*aryl-C*), 61.0 (*C*H_2), 55.6 (O*C*H_3), 42.2 (N*C*H_3), 34.4, 35.1 (*C*(CH_3)$_3$), 29.6, 31.8 (C(*C*H_3)$_3$). MS (electrospray ionisation): *m*/*z* 432.2 $[M + H]^+$.

Preparation of complex 5. Compound **3** (0.30 g, 0.91 mmol) was taken up in 15 mL of dichloromethane and was added dropwise to $TiCl_4$(thf)$_2$ (0.30 g, 0.91 mmol) in 15 mL of dichloromethane at −95 °C with vigorous stirring. Upon complete addition the acetone/liquid nitrogen slurry was removed and the reaction mixture was allowed to return to room temperature. The orange solution was stirred overnight. The volatiles were removed *in vacuo* and the resulting orange solid was washed with 2 × 10 mL of petroleum spirits before being dried under reduced pressure to give **5** as an orange powder in 74% yield (0.28 g, 0.67 mmol). Large orange needles suitable for X-ray diffraction were grown by evaporation of a dichloromethane solution of **5**. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.33 (s, 1H, N=C*H*), 7.66 (dd, *J* = 1.50, 6.60 Hz, 1H, *aryl-H*), 7.47 (dd, *J* = 1.50, 6.60 Hz, 1H, *aryl-H*), 7.19 (t, *J* = 7.80 Hz, 1H, *aryl-H*), 4.41 (s, 3H, CH_2–O–C*H*$_3$), 4.27 (s, 2H, C*H*$_2$–O–CH_3), 1.53 (s, 6H, C(C*H*$_3$)$_2$), 1.51 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 162.5 (N=*C*H), 127.4, 137.3, 160.7 (*aryl-C*$_{ipso}$), 125.2, 133.6, 134.6 (*aryl-C*), 86.2 (CH_2–O–*C*H_3), 68.8 (*C*H_2–O–CH_3), 66.1 (*C*(CH_3)$_2$), 35.5 (*C*(CH_3)$_3$), 29.8 (C(*C*H_3)$_3$), 27.2 (C(*C*H_3)$_2$). Anal. Calcd for $C_{16}H_{24}NO_2TiCl_3$: C 46.13, N 3.36, H 5.81. Found: C 46.39, N 3.31, H 5.68.

Preparation of complex 6. Titanium(IV) tetrachloride (0.15 g, 0.81 mmol) in 10 mL of toluene was cooled to −95 °C with vigorous stirring. To the resulting bright orange solution was added dropwise a solution of **4** (0.32 g, 0.73 mmol) in 5 mL of toluene. Upon complete addition the resulting dark red solution was allowed to return to room temperature and stirred overnight. The volatiles were removed *in vacuo* and the resulting dark red powder was dried for one hour. The powder was washed with 3 × 5 mL of petroleum spirits and dried to give the title compound in 80% yield (0.36 g, 0.58 mmol). Crystals suitable for X-ray crystallography were grown by evaporation of a dichloromethane solution of **6**. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.05 (bs, 1H, N^+–*H*–O^-), 7.79 (m, 2H, *aryl-H*), 7.62 (m, 1H, *aryl-H*), 7.37–7.44 (m, 3H, *aryl-H*), 6.99 (d, *J* = 8.1 Hz, 1H, *aryl-H*), 6.78 (t, *J* = 7.5 Hz, 1H, *aryl-H*), 5.97 (m, 2H, *aryl-H*), 5.70 (dd, *J* = 2.1, 12.8 Hz, 1H, C*H*$_2$), 4.28 (dd, *J* = 9.9, 12.8 Hz, 1H, C*H*$_2$), 3.79 (s, 3H, OCH_3), 3.75 (d, *J* = 5.1 Hz, 3H, N*C*H_3), 1.43 (s, 9H, C(C*H*$_3$)$_3$), 1.04 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR

(CD_2Cl_2, 75.41 MHz): δ 170.1 (*O aryl-C*$_{ipso}$), 121.2, 122.0, 134.9, 138.0, 140.8, 147.3, 155.4 (*aryl-C*$_{ipso}$), 112.4, 120.4, 122.4, 127.4, 127.8, 130.7, 130.8, 131.4, 131.9, 133.1 (*aryl-C*), 62.3 (CH_2), 56.0 (OCH_3), 47.4 (NCH_3), 34.9, 36.1 ($C(CH_3)_3$), 31.2, 31.4 ($C(CH_3)_3$). Anal. Calcd for $C_{29}H_{37}NO_2TiCl_4$: C 56.06, N 2.25, H 6.01. Found: C 55.22, N 1.75, H 5.39.

Preparation of complex 7. To titanium(IV) tetrachloride (0.6 mL, 0.49 mmol) in 10 mL of toluene at −95 °C was added dropwise compound **2** (0.26 g, 0.44 mmol) in 6 mL of toluene. The dark red solution was allowed to return to room temperature and stirred overnight. The volatiles were removed *in vacuo* and the resulting dark red honeycomb was crushed into a powder which was washed with 3 × 10 mL of petroleum spirits. The solid was then dissolved in dichloromethane, filtered and dried *in vacuo*. The dark red solid was then dissolved in diethyl ether and a red powder was precipitated *via* layering with petroleum spirits. Isolation of the solid *via* filtration gave the title compound in 70% yield (0.20 g, 0.31 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.73 (bs, 1H, *H*–O), 8.03 (s, 1H, N=C*H*), 7.04–7.52 (m, 10H, *aryl-H*), 2.62 (s, 3H, SCH_3), 2.31 (s, 3H, aryl-CH_3), 2.12–2.17 (m, 9H, adamantly-C*H*), 1.85 (m, 6H, adamantly-C*H*). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 193.6 (N=*C*H), 123.9, 124.6, 124.7, 127.3, 128.8, 129.0, 129.1, 130.3, 131.1, 132.7, 132.9, 134.4, 136.9, 139.9, 140.1 (*aryl-C*), 28.5, 36.2, 39.6, 39.8 (*adamantly-C*), 19.8 (Ar-CH_3), 14.6 (SCH_3). Anal. Calcd for $C_{31}H_{33}NOSTiCl_4$: C 56.64, N 2.13, S 4.88, H 5.06. Found: C 56.62, N 2.07, S 5.19, H 4.88.

Ethylene polymerisation/oligomerisation

A 0.3 L stainless steel Parr 5500 Compact Mini Reactor was preheated to 120 °C and flushed with four vacuum/argon cycles and two ethylene purges. The reactor was cooled to the appropriate temperature and charged with toluene (total solvent volume of 50 mL). The catalyst (20 μmol) in 10 mL of toluene was then activated, in a Schlenk to observe any colour changes, with 300 equivalents of MAO before injection into the reactor. During the reaction, the pressure was kept constant with a replenishing flow of ethylene. After 30 minutes run time the replenishment of ethylene was ceased and the reactor cooled to <10 °C before purging of excess ethylene to atmospheric pressure and injection of a weighed amount of nonane standard. Residual MAO was quenched with ~10% HCl solution and samples of the reaction mixture were taken for analysis and quantification of soluble analytes *via* GC and where appropriate GC-MS. Any polymer formed was removed *via* filtration and washed with 10% HCl and methanol before drying at ~60 °C for 3 days.

X-ray crystallography

Data for **4–6** and S1† were collected at −173 °C on crystals mounted on a Hampton Scientific cryoloop at the MX1 beamline of the Australian Synchrotron.[58] The structures were solved by direct methods with SHELXS-97, refined using full-matrix least-squares routines against F^2 with SHELXL-97,[59] and visualised using X-SEED.[60] All non-hydrogen atoms were refined anisotropically. Disordered lattice solvent was apparent for **5** which could be modelled as a two site complementary occupancy of DCM with common chloride. Disordered toluene lattice solvent was apparent for **6**, residing on 4bar symmetry sites, and was similarly modelled. Details of the disorder modelling are provided in the cif files. Ammonium, imminium and phenolic protons were located and positionally refined in the cases of **4** and **6**. All other hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C–H distances of 0.95 Å (sp^2CH), 0.99 Å (CH_2), 0.98 Å (CH_3). The thermal parameters of all hydrogen atoms were estimated as U_{iso}(H) = 1.2U_{eq}(C) except for CH_3 where U_{iso}(H) = 1.5U_{eq}(C). A summary of crystallographic data given below.

Crystal data for 4. $C_{29}H_{37}NO_2$, M = 431.60, monoclinic, a = 26.9936(15), b = 10.4290(19), c = 18.5420(17) Å, β = 107.509(4)°, U = 4978.0(11) Å^3, T = 100 K, space group $C2/c$ (no. 15), Z = 8, 41 288 reflections measured, 6157 unique (R_{int} = 0.0323), 5469 > 4$\sigma(F)$, R = 0.0486 (observed), R_w = 0.1321 (all data). Crystal data for **5**: $C_{16}H_{24}Cl_3NO_2Ti{\cdot}1/2(CH_2Cl_2)$, M = 459.07, triclinic, a = 8.1970(18), b = 16.344(3), c = 16.526(2) Å, α = 90.003(2), β = 103.428(5) γ = 103.650(7)°, U = 2089.1(7) Å^3, T = 100 K, space group $P\bar{1}$ (no. 2), Z = 4, 28 454 reflections measured, 7664 unique (R_{int} = 0.0250), 7257 > 4$\sigma(F)$, R = 0.0796 (observed), R_w = 0.2232 (all data). Crystal data for **6**: $C_{29}H_{37}Cl_4NO_2Ti{\cdot}5/4(C_7H_8){\cdot}CH_2Cl_2$, M = 821.39, tetragonal, a = 22.585(2), c = 16.1750(18) Å, U = 8250.7(14) Å^3, T = 100 K, space group $I\bar{4}$ (no. 82), Z = 8, 68 917 reflections measured, 10 587 unique (R_{int} = 0.0568), 9354 > 4$\sigma(F)$, R = 0.0433 (observed), R_w = 0.1127 (all data). Crystal data for S1:† $C_{24}H_{34}Cl_4N_2O_4Ti$, M = 604.23, triclinic, a = 8.3590(9), b = 9.5330(5), c = 10.1630(5) Å, α = 86.070(5), β = 67.242(6), γ = 67.192(6)°, U = 685.24(9) Å^3, T = 100 K, space group $P\bar{1}$ (no. 2), Z = 1, 7522 reflections measured, 1945 unique (R_{int} = 0.0204), 1869 > 4$\sigma(F)$, R = 0.0281 (observed), R_w = 0.0677 (all data).

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Notes and references

1 T. Agapie, *Coord. Chem. Rev.*, 2011, **255**, 861.
2 A. W. Al-Sa'doun, *Appl. Catal., A*, 1993, **105**, 1–40.
3 Y. Chauvin and H. Olivier, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and

W. A. Herrmann, VCH, Weinheim, 1996, vol. 1, pp. 258–268.
4 J. T. Dixon, M. J. Green, F. M. Hess and D. H. Morgan, *J. Organomet. Chem.*, 2004, **689**, 3641.
5 D. S. McGuinness, *Chem. Rev.*, 2011, **111**, 2321.
6 P. W. N. M. van Leeuwen, N. D. Clément and M. J.-L. Tschan, *Coord. Chem. Rev.*, 2011, **255**, 1499.
7 G. P. Belov, *Pet. Chem.*, 2012, **52**, 139.
8 D. F. Wass, *Dalton Trans.*, 2007, 816.
9 Y. Suzuki, S. Kinoshita, A. Shibahara, S. Ishii, K. Kawamura, Y. Inoue and T. Fujita, *Organometallics*, 2010, **29**, 2394.
10 P. J. W. Deckers, B. Hessen and J. H. Teuben, *Angew. Chem., Int. Ed.*, 2001, **40**, 2516.
11 P. J. W. Deckers, B. Hessen and J. H. Teuben, *Organometallics*, 2002, **21**, 5122.
12 H. Hagen, W. P. Kretschmer, F. R. van Buren, B. Hessen and D. A. van Oeffelen, *J. Mol. Catal. A: Chem.*, 2006, **248**, 237.
13 B. Hessen, *J. Mol. Catal. A: Chem.*, 2004, **213**, 129.
14 J. Huang, T. Wu and Y. Qian, *Chem. Commun.*, 2003, 2816.
15 M. Mitani, T. Nakano and T. Fujita, *Chem.–Eur. J.*, 2003, **9**, 2396.
16 T. Matsugi and T. Fujita, *Chem. Soc. Rev.*, 2008, **37**, 1264.
17 Y. Nakayama, J. Saito, H. Bando and T. Fujita, *Chem.–Eur. J.*, 2006, **12**, 7546.
18 (*a*) M. Mitani, J. Saito, S. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka and T. Fujita, *Chem. Rev.*, 2004, **4**, 137; (*b*) H. Makio, H. Terao, A. Iwashita and T. Fujita, *Chem. Rev.*, 2011, **111**, 2363.
19 A. Sukuma, M.-S. Weiser and T. Fujita, *Polym. J.*, 2005, **39**, 193.
20 H. Makio and T. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1532.
21 J. Tian, P. D. Hustad and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 5134.
22 P. D. Hustad, J. Tian and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 3614.
23 D. Owiny, S. Parkin and F. T. Ladipo, *J. Organomet. Chem.*, 2003, **678**, 134.
24 D. A. Pennington, D. L. Hughes, M. Bochmann and S. J. Lancaster, *Dalton Trans.*, 2003, 3480.
25 D. A. Pennington, W. Clegg, S. J. Coles, R. W. Harrington, M. B. Hursthouse, D. L. Hughes, M. E. Light, M. Schormann, M. Bochmann and S. J. Lancaster, *Dalton Trans.*, 2005, 561.
26 J. Lee, Y. Kim and Y. Do, *Inorg. Chem.*, 2007, **46**, 7701.
27 R. Cariou, V. C. Gibson, A. K. Tomov and A. J. P. White, *J. Organomet. Chem.*, 2009, **694**, 703.
28 M.-L. Gao, Y.-F. Gu, C. Wang, X.-L. Yao, X.-L. Sun, C.-F. Li, C.-T. Qian, B. Liu, Z. Ma, Y. Tang, Z. Xie, S.-Z. Bu and Y. Gao, *J. Mol. Catal. A: Chem.*, 2008, **292**, 62.
29 X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z. Wang, Z. Xie and Y. Tang, *Angew. Chem., Int. Ed.*, 2009, **48**, 8099.
30 K. Cui, B. Liu, C. Wang, J.-Y. Yu and Z. Ma, *J. Mol. Catal. A: Chem.*, 2007, **266**, 93.
31 Y. Wang, W. Zhang, W. Huang, L. Wang, C. Redshaw and W.-H. Sun, *Polymer*, 2011, **52**, 3732.
32 W.-Q. Hu, X.-L. Sun, C. Wang, Y. Gao, Y. Tang, L.-P. Shi, W. Xia, J. Sun, H.-L. Dai, X.-Q. Li, X.-L. Yao and X.-R. Wang, *Organometallics*, 2004, **23**, 1684.
33 C. Wang, Z. Ma, X.-L. Sun, Y. Gao, Y.-H. Guo, Y. Tang and L.-P. Shi, *Organometallics*, 2006, **25**, 3259.
34 G. Paoluccia, A. Zanella, L. Sperni, V. Bertolasi, M. Mazzeo and C. Pellecchia, *J. Mol. Catal. A: Chem.*, 2006, **258**, 275.
35 M.-L. Gao, X.-L. Sun, Y.-F. Gu, X.-L. Yao, C.-F. Li, J.-Y. Bai, C. Wang, Z. Ma, Y. Tong, Z. Xie, S.-Z. Bu and C. Qian, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 2807.
36 C. Wang, X.-L. Sun, Y.-H. Guo, Y. Gao, B. Liu, Z. Ma, W. Xia, L.-P. Shi and Y. Tang, *Macromol. Rapid Commun.*, 2005, **26**, 1609.
37 M. Gao, C. Wang, X. Sun, C. Qian, Z. Ma, S. Bu, Y. Tang and Z. Xie, *Macromol. Rapid Commun.*, 2007, **28**, 1511.
38 *WO Pat.*, 005003 A1 (Mitsui Chemicals, Inc), 2009.
39 D. C. H. Oakes, B. S. Kimberley, V. C. Gibson, D. J. Jones, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2004, 2174.
40 D. C. H. Oakes, B. S. Kimberley, V. C. Gibson, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2006, **45**, 3476.
41 M. Lamberti, M. Bortoluzzi, G. Paolucci and C. Pellecchia, *J. Mol. Catal. A: Chem.*, 2011, **351**, 112.
42 A. Cohen, J. Kopilov, I. Goldberg and M. Kol, *Organometallics*, 2009, **28**, 1391.
43 D. M. Goedde and G. S. Girolami, *Inorg. Chem.*, 2006, **45**, 1380.
44 K. E. du Plooy, U. Moll, S. Wocadlo, W. Massa and J. Okuda, *Organometallics*, 1995, **14**, 3129.
45 R. Fandos, B. Gallego, M. I. López-Solera, A. Otero, A. Rodríguez, M. J. Ruiz, P. Terreros and T. van Mourik, *Organometallics*, 2009, **28**, 1329.
46 T. J. Boyle, R. M. Sewell, L. A. M. Ottley, H. D. Pratt III, C. J. Quintana and S. D. Bunge, *Inorg. Chem.*, 2007, **46**, 1825.
47 S. Friedrich, L. H. Gade, A. J. Edwards and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1993, 2861.
48 J. Strauch, T. H. Warren, G. Erker, R. Frolich and P. Saarenketo, *Inorg. Chim. Acta*, 2000, **300–302**, 810.
49 A.-Q. Jia and G.-X. Jin, *Dalton Trans.*, 2009, 8838.
50 G. Alesso, M. Sanz, M. E. G. Mosquera and T. Cuenca, *Eur. J. Inorg. Chem.*, 2008, 4638.
51 R. K. J. Bott, D. L. Hughes, M. Schormann, M. Bochmann and S. J. Lancaster, *J. Organomet. Chem.*, 2003, **665**, 135.
52 J. A. Suttil, D. S. McGuinness, M. G. Gardiner and S. J. Evans, *Dalton Trans.*, 2013, DOI: 10.1039/c3dt32183e.
53 M. K. Mahanthappa, A. P. Cole and R. M. Waymouth, *Organometallics*, 2004, **23**, 836.
54 P. C. Wailes, R. S. P. Coutts and H. Weigold, *Organometallic Chemistry of Titanium, Zirconium and Hafnium*, Academic Press, New York, 1974, ch. 6, pp. 196–227.

55 J. J. Eisch, S. I. Pombrik and G.-X. Zheng, *Organometallics*, 1993, **12**, 3856.
56 T. Wada, T. Taniike, I. Kouzai, S. Takahashi and M. Terano, *Macromol. Rapid Commun.*, 2009, **30**, 887.
57 J. A. Suttil, D. S. McGuinness, M. Pichler, M. G. Gardiner, D. H. Morgan and S. J. Evans, *Dalton Trans.*, 2012, **41**, 6625.
58 T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerly, S. M. Soltis and P. Kuhn, *J. Synchrotron Radiat.*, 2002, **9**, 401.
59 G. M. Sheldrick, *SHELX97, Programs for Crystal Structure Analysis*, Universität Göttingen, Germany, 1998.
60 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.

